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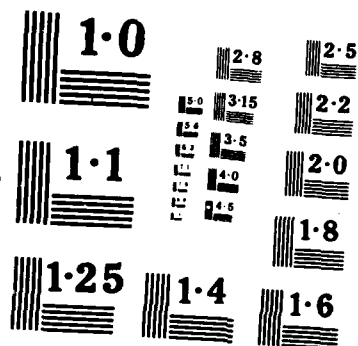
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by  
R.D. Miller

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Chemistry

# Research Report

SILICON CONTAINING PHOTORESISTS

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## SILICON CONTAINING PHOTORESISTS

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**ABSTRACT:** The problems created by the generation of small features over topography has focussed attention on multilayer techniques in spite of the added processing complexities. Particularly attractive in this regard are those processes employing oxygen reactive ion etching ( $O_2$ -RIE) for image transfer because of the intrinsically anisotropic nature of the transfer process. This technique requires polymeric materials which are stable to  $O_2$ -RIE conditions. This requirement has stimulated the development of organometallic resists particularly those containing silicon which produce etch resistant refractory oxides in the oxygen plasma environment. Recent advances in the development of silicon containing resists for multilayer applications are reviewed.

Most of the patterning for current electronic circuitry is accomplished using photolithographic techniques (1). Using this procedure, a substrate (usually silicon) is coated with a layer of photoresist and exposed through a mask to produce a latent image. The image is then developed with an appropriate solvent to generate the desired relief pattern. Photoresists are classified as either positive or negative functioning depending on whether the exposed area becomes more or less soluble in the developer. Negative resists are usually materials (often containing unsaturation) where polymer chain crosslinking or other types of interchain reactions occur upon exposure, thus greatly reducing the solubility of the exposed areas. These materials frequently show high sensitivity due to the gain inherent in photopolymerization processes, but are often resolution limited due to the swelling of the resist patterns during development. Recently, some negative resists which function by changes in the polarity of the material in the exposed areas rather than by crosslinking have been described (2-4). These materials are less prone to swelling and are useful for the generation of high resolution patterns.

The vast majority of the commercial positive photoresists are comprised of a base soluble Novolac type resin (Cresol-formaldehyde condensation polymers) and a sensitizer which is usually a substituted derivative of 1,2-naphthoquinone-2-diazide (5). The hydrophobic sensitizer inhibits the dissolution of the matrix resin in base prior to exposure. After exposure, the sensitizer is converted into a substituted indene carboxylic acid which greatly increases the rate of dissolution of the resin in the exposed regions. The combination of these effects results in a large difference in solubility between the exposed and unexposed regions which is responsible for the facile development of the latent mask image. Since the dissolution process in dilute base is a result of chemical reaction between the basic developer and the weakly acidic Novolac resin, it proceeds with very little swelling. Positive resists of this type are hence intrinsically capable of high resolution, although their sensitivity is often much lower than that observed for negative resists.

The current drive toward higher density circuitry requires smaller features and consequently higher resolution lithographic techniques. As the industry moves toward smaller lateral geometries, the aspect ratio (height/width) of the features increase because the resist thickness in a single layer process is limited by the necessary coverage of chip topography. The generation of small, high aspect ratio features often requires near vertical wall profiles. This sometimes creates problems using the classical single layer positive resists because the wet development process is intrinsically isotropic (*i.e.*, there is some lateral as well as vertical development) which can erode the pattern profile. There are also additional problems with single layer resists which are associated with precise line width control for small features generated over significant chip topography (6). This is caused by light scattering from edges and corners of the topographic features coupled with problems of exposure homogeneity exacerbated by the differing resist thicknesses resulting from the topography. In addition, for monochromatic radiation, standing waves in the variable thickness resist coating can also cause linewidth control problems.

In an effort to circumvent some of the problems caused by chip topography, a number of multilayer resist schemes have been introduced (6). The simplest of these is the imagable bilayer illustrated in Figure 1. In this scheme, the chip containing any surface topography is coated with a thick planarizing polymer layer. Many materials can be used for this purpose (*e.g.*, PMMA, polyimides, hardbaked photoresist, *etc.*) and the selection is dictated by specific process requirements. This layer is then overcoated with a thin (0.1-0.2  $\mu\text{m}$ ) layer of an imagable material. The top layer is imaged with high resolution in the normal fashion and the pattern developed usually by wet development techniques. The thinness of this layer allows the generation of high resolution patterns even using wet development processes. These patterns can then be transferred into the planarizing layer either by deep UV flood exposure utilizing the masking characteristics of the resist layer or by oxygen reactive ion etching ( $\text{O}_2$ -RIE). The former requires that the remaining resist layer effectively mask the underlying layer



from exposure and that the planarizing layer is itself UV sensitive. This process also requires a subsequent wet development step for the imaged, planarizing layer with its attending drawbacks. Alternatively, the image can be transferred by oxygen plasma etching techniques. This procedure is attractive because it is dry (no solvents), alleviates adhesion problems and, most importantly, the etching process can be controlled so that it is highly anisotropic. In this manner, high aspect ratio patterns with near vertical wall profiles can be produced.

Transfer of patterns by  $O_2$ -RIE does, however, place some unique demands on the thin imaging layer. Not only must it be patternable with high resolution, but it must also be much more stable under the etching conditions than the underlying planarizing polymer. The latter criterion is admirably satisfied by organometallic polymers which contain elements (Si, Ti, B, Sn, Al, *etc.*) which form refractory oxides in an oxygen plasma (7). Since a large number of silicon containing polymers are known and  $SiO_2$  forms a good oxygen etch barrier, these materials have received considerable attention for multilayer applications (8).

The question of just how much silicon must be present to create a suitable oxygen etch barrier has been answered recently by a number of groups working on silicon containing copolymers (4,9). The etch resistance of the investigated copolymers varies nonlinearly with the amount of silicon, but materials which contain at least 10% by weight seem to form effective oxygen etch barriers. The relative effectiveness of these materials seems also to depend somewhat on etching conditions such as power, voltage bias and oxygen pressure.

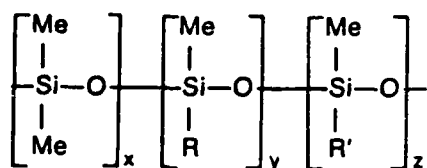
The silicon in a photoresist formulation may be simplistically viewed as playing either passive or active role. We define a passive role as one where a silicon containing monomer or polymer is utilized solely for the purpose of providing oxygen etch resistance and is not transformed during the exposure. In either role the silicon may be

present as a pendant polymer substituent, be incorporated into the polymer backbone or it may simply be a monomer additive.

### Silicon Containing Negative Resists

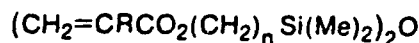
Since silicon containing polymers are often prone to radiation induced crosslinking during irradiation, it is not surprising that the first reports of such materials for multilayer lithographic applications were as negative resists. In this regard, Hatzakis and co-workers (10) showed that the siloxane terpolymer **1** crosslinked upon exposure to light or ionizing radiation and etched very slowly under O<sub>2</sub>-RIE conditions. The low glass transition temperature (T<sub>g</sub>) of this material requires the use of very thin films to prevent thermal deformation of the imaged structures upon processing. Workers at Nippon Telephone and Telegraph (NTT) subsequently showed that poly(diphenylsiloxane) which has a much higher T<sub>g</sub> could be partially chloromethylated to yield a polymer which readily crosslinked upon deep UV ( $\lambda$  220-280 nm) exposure (11).

An "all dry" process (no wet development step) for X-ray exposure has been reported by Taylor *et al.* (12,13) who incorporated bifunctional silicon containing acrylates such as **2** into the radiation sensitive matrix polymer poly(2,3-dichloro-1-propylacrylate). X-ray exposure produces radical sites which subsequently polymerize and lock the silicon containing monomer into the polymer matrix. The exposed resist was then baked to volatilize the unreacted monomer in the unexposed regions and the patterns developed by O<sub>2</sub>-RIE. Using this technique, high resolution submicron patterns were created. One drawback is that the resist has relatively low contrast (*i.e.*, poor etch rate differential between the exposed and unexposed regions) because all or most of the unreacted monomer must be thermally removed from the unexposed regions prior to pattern transfer.



R = Ph, R' = vinyl

1

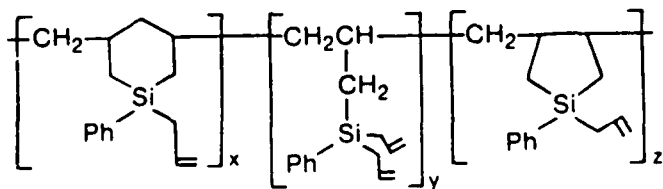


2 R = H, Me

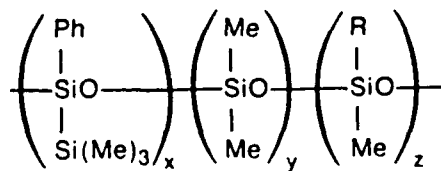
n = 4

A number of negative resists where silicon is incorporated as a pendant substituent have also been reported. In this regard, since both p-chloro and p-chloromethyl polystyrene crosslink readily upon deep UV irradiation (5), it is not surprising that copolymers of these respective styrene monomers with p-trimethylsilylstyrene (14,15) also function as negative resists for bilayer applications. These systems offer the advantage that the oxygen etch stability of the copolymers can be varied by changes in the copolymer composition.

A somewhat different approach was adopted by Saigo and co-workers (16) who found that phenyl triallylsilane could be polymerized to yield a linear polymer 3 containing pendant allylic functionality. The unsaturated groups could then be utilized for crosslinking by irradiation in the presence of appropriate photocrosslinking reagents such as aryl bis azides.



3



R = vinyl, allyl

4

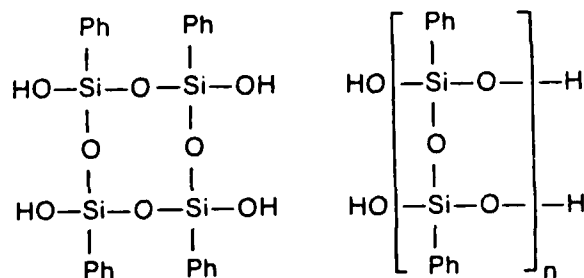
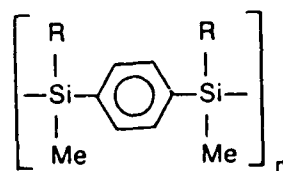
Recently, Ishikawa *et al.* (17) have reported a new class of negative resists 4 which contain both pendant and backbone silicon. These materials undergo crosslinking through silyl radicals produced by side chain scission of the disilanyl units.

### Silicon Containing Positive Resists

Considerable effort has been focused recently on silicon containing materials which function as positive resists. Many of these contain pendant silicon functionality which often plays a passive role. The generation of silicon containing Novolac-type resins represents one such effort. Workers at AT&T Bell Labs have prepared a number of base soluble Novolacs by the condensation of formaldehyde with a mixture of either phenol-m-trimethylsilylphenol (18) or more recently with m-cresol-p-trimethylsilylmethyl phenol (18). The monomer proportions were adjusted to produce resins with a silicon content of ~9% or more while maintaining the solubility in dilute base. Related resins have also been described by workers at NEC from m-trimethylsilylalkoxyphenol, 2-methyl resorcinol and formaldehyde (20). The silylated Novolac type resins were designed for use with substituted 1,2-naphthoquinone-2-diazide sensitizers employed in classical photoresist formulations. The silylated Novolac resists have the obvious advantage that they can be used with conventional mercury light sources available in commercial projection scanning and step-and-repeat lithographic tools. A potential drawback of these materials is, however, that the etch resistance is, in some cases, barely adequate and they are not suitable for use with shorter wavelength (*e.g.*, deep UV) exposure sources. Workers at Hitachi (21) have recently described a related system composed of a Novolac-type resin containing a soluble, nonvolatile, base soluble silicon additive. The additive 5 was a mixture of the cis-1,3,5,7-tetrahydroxy 1,3,5,7-tetraphenylcyclotetrasiloxane and a commercially available polyphenylsilsequioxane. An interesting variation of the silylated Novolac approach for the production of negative relief images has recently been reported by Coopmans *et al.* (22). This procedure exploits the observation that certain Novolac-1,2-naphthoquinone 2-diazide formulations are resistant to silylation by reagents such as hexamethyldisilazane (HMDS) prior to exposure. After irradiation, the phenolic hydroxyl functionality in the exposed regions is rapidly silylated under the processing conditions to produce an oxygen etch barrier. An "all dry" process capable of submicron resolution in a single layer of resist has been described (22).

Other positive, silicon containing resists where silicon plays a more active role have also been described. For example, an oxygen etch resistant, deep UV sensitive copolymer with pendant silicon composed of trimethylsilylmethyl methacrylate and 3-oximino-2-butanone methacrylate units has been reported (8). The former comonomer provides improved etch resistance while the latter is used to enhance the resist sensitivity to deep UV radiation.

A number of radiation sensitive positive resists which contain silicon in the backbone have also been reported. In this regard, workers at Hitachi (23,24) have reported that polymeric disilanes such as 6 generated by the condensation of substituted bis-chlorosilyl benzenes with alkali metals function in a positive fashion. Chain breaks results from the photoscission of the disilanyl units. These materials absorb strongly in the deep UV and also form excellent oxygen etch barriers.

5

R = Me, Et, Ph

6

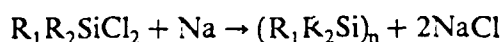
Recently, a new class of radiation sensitive materials which contain only silicon in the backbone has been described. The unusual spectroscopic properties and radiation sensitivity of these polysilanes have resulted in many new applications including a number in microlithography. The unusual characteristics of the polysilanes have created considerable interest recently and will be discussed in some detail.

### Polysilanes

Substituted silane polymers were probably first synthesized over 40 years ago (25). The early materials were highly crystalline and insoluble because of the nature of pendant substituents. These undesirable properties are not characteristic of this general

class of polymers and recent synthetic efforts have generated a large number of soluble, high molecular weight homo and copolymers (26). The ready availability of soluble polymers from which high quality films can be cast has stimulated an intensive investigation of these materials. From these studies have emerged a variety of new applications including their use in multilayer microlithography (27-30).

High molecular weight linear polysilanes can be produced by a Wurtz type condensation of the respective substituted dichlorosilanes as shown below. In this regard sodium dispersion seems most effective for the production of the linear polymers. The yields in this process are dependent on structure and range from 5-70%. The use of lithium usually results in cyclic oligomers (26)



Despite the fact that the backbone bonding in these materials is predominantly sigma in nature, the extensively catenated silicon derivatives absorb strongly in the UV-visible region (26). In this regard, both the  $\lambda_{max}$  and the  $\epsilon/SiSi$  depend on molecular weight, both increasing rapid at first and approaching limiting values at a degree of polymerization of around 40-50 (31). The molar absorptivities of these materials are very large and range from 4000-25000 per silicon-silicon bond depending on the nature and position of the substituents. Alkyl derivatives absorb strongly around 300-325 nm with sterically demanding substituents causing significant red shifts (see Figure 3). Aryl substituents directly bonded to silicon cause strong red shifts of 25-40 nm because of the electronic interaction of the substituents with the sigma bonded framework (32). Recently, we have demonstrated by studies in the solid state that the position and intensity of the absorption maxima also depends on the conformation of the polymer backbone (33-35). In this regard, it was observed that a planar zigzag conformation causes a red shift of over 55 nm relative to observed solution values where the backbone is presumably disordered and the polymer has been shown by light scattering to adopt a random coil configuration (36). In the solid state, deviations by

as little as  $30^\circ$  from a trans coplanar conformation even in a regular structure results in blue shifts of  $\sim 60$  nm in the absorption spectrum (37). Furthermore, a recent prediction based on conformation calculations suggests that polysilanes with large substituents may actually prefer a helical configuration rather than planar zigzag (38,39) and that in most cases strong solid state intermolecular interactions are necessary before the latter conformation predominates.

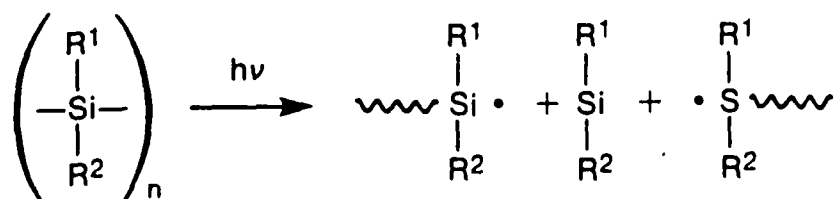
Interestingly, soluble symmetrical diaryl polysilanes are the most red shifted of all known polysilane derivatives and absorb around 400 nm (40). The magnitude of this shift far exceeds that anticipated by electronic substituent predictions which suggests that it might also be conformational in origin. In this regard, we have tentatively proposed that these materials may contain extended planar zigzag segments even in solution.

### Photochemistry

Since both the  $\lambda_{\max}$  and  $\epsilon_{\text{SiSi}}$  are dependent on molecular weight (31), processes which reduce the molecular weight should lead to a bleaching of the original absorption. We have observed this phenomenon for all of the polysilanes examined although the bleaching rate varies with structure. Photobleaching of a film of a typical polysilane is shown in Figure 3. Bleaching of the original absorption both in solution and in the solid state is associated with the formation of lower molecular weight fragments as determined by gpc analysis of the irradiated samples. In this regard, gpc analysis of irradiated samples of alkyl polysilanes show little indication of crosslinking while similar studies on irradiated samples of aromatic derivatives such as poly(phenyl methylsilane) indicates that a higher molecular weight portion remains. The quantum yields for scission ( $\Phi_s$ ) and crosslinking ( $\Phi_x$ ) for irradiated polymers can be determined routinely from plots of  $1/\overline{M}_n$  and  $1/\overline{M}_w$  versus dose (41). Using this technique we have determined that the quantum yields for scission for alkyl substituted polysilanes in solution are high and range from  $\sim 0.5$ -1.0 depending on the nature of the substituents. Similarly high values are obtained for aryl derivatives, but in these cases a competitive crosslinking component

is often observed. ( $\Phi_x \sim 0.12-0.18$ ). In spite of this the aryl derivatives are still predominantly scissioning polymers in solution and  $\Phi_s/\Phi_x$  values of 5-7 are observed. In all cases, the quantum yields for both processes decrease significantly (>50 fold) in going from solution to the solid state presumably because solid state cage effects would be expected to promote chain repair (*vide infra*).

Exhaustive irradiation of high molecular weight polysilane derivatives at 254 nm in the presence of trapping reagents such as triethyl silane or alcohols lead to products which indicate that both substituted silylenes and silyl radicals are produced as intermediates (42). The isolation of these products suggests that the photochemical pathways observed for the high polymers may be similar to those proposed in mechanistic studies of the photodecomposition of shorter acyclic silicon catenates (43,44). Other authors have also suggested, on the basis of mass spectroscopic studies, that substituted silylenes are produced in the photovolatilization of some polysilane copolymers upon deep UV exposure (45). On the basis of the accumulated evidence, we propose a basic mechanism shown below for the photodecomposition of substituted silane polymers which not only accommodates the proposed intermediates, but is consistent with the decreased efficiency in the solid state. While the proposed mechanism is consistent with the limited data, it has not been determined whether the silylenes arise from the photolysis of the polymer itself and/or are produced in a subsequent decomposition of the silyl radicals. In the case of the polymers is assumed that silyl radicals disproportionation, which has been demonstrated to be a facile reaction for trimethyl silyl radicals themselves (46), is competitive with chain repair.





## Polysilanes in Photolithography

The intense optical absorption over an extended spectral range, ready bleachability and oxygen reactive ion etch stability displayed by the polysilanes suggest a number of photomicro lithographic applications (27-31,45). To date, we have exercised these materials as short wavelength contrast enhancing materials and as imagable etch barriers in bilevel processes. In the latter application, we have demonstrated feasibility both with processes utilizing wet development of the imaged layer as well as in an "all dry" process where the initial image is produced by excimer laser ablation of the polysilane (30).

Contrast enhancement lithography is a clever procedure which utilizes a thin, strongly absorbing but bleachable contrast enhancing material coated over a classical photoresist to sharpen the diffraction distorted mask image at photoresist surface. The result is greatly improved optical pattern resolution. The mechanism by which the image quality is improved is too complicated to discuss here and the interested reader is referred to the pertinent references (47,48).

Most commercial contrast enhancing materials are designed to operate in the near UV-visible range. Certain polysilane derivatives possess all of the necessary features to provide contrast enhancement in the mid (300-340 nm) and deep UV (220-280 nm) regions thus allowing the utilization of the improved resolution intrinsic to short wavelength exposure sources. Particularly significant in this regard is their strong absorption and excellent bleachability at short wavelengths which are essential for the process. Accordingly, we have demonstrated this principle for mid UV projection printing using a nonoptimized polysilane contrast enhancing layer coated over a commercial mid UV photoresist and the results are shown in Figure 4 (28). The figure clearly demonstrates that there is less thinning of the control resist line for the contrast enhanced process relative to the conventional process.

We have also demonstrated the utility of polysilanes in a number of mid UV bilayer processes. Figure 5 shows submicron features printed in a thin layer of

poly(cyclohexylmethylsilane) and transferred by  $O_2$ -RIE (29). In this case the polysilane image was wet developed with isopropanol prior to the image transfer. The image quality and vertical wall profiles clearly shows the utility of polysilane derivatives. In an extension of this work, we have also demonstrated submicron capability for an "all dry" bilayer process. In this case, the polysilane imaging layer was first photoablated using a KrF excimer laser (55 mJ/cm<sup>2</sup>-pulse, 550 mJ total dose at 248 nm) (30,49). The clean images produced in this step were subsequently transferred into the thick planarizing layer using  $O_2$ -RIE techniques.

In summary the demands for improved resolution over complex chip topography has resulted in studies of multilayer lithographic processes particularly those using  $O_2$ -RIE techniques for image transfer. This has resulted in a greatly increased interest in imagable organometallic resists especially those containing silicon. Although many of the initial efforts have centered on negative resists there has been recent progress in the development of new silicon containing positive resists. In this regard, the polysilane derivatives which represent a new class of radiation sensitive,  $O_2$ -RIE resistant polymers, show considerable promise and versatility.

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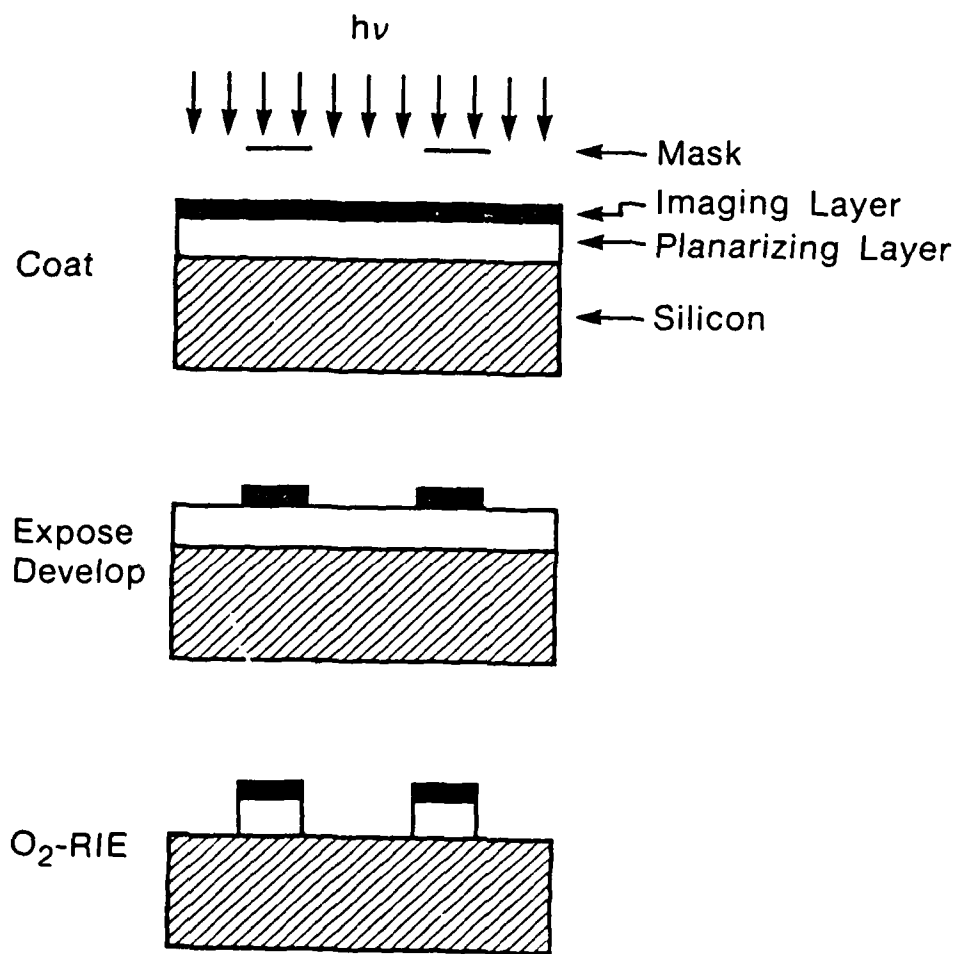
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## Bilayer Process



**Figure 1.** A typical bilayer lithographic scheme utilizing oxygen reactive ion etching for image transfer.

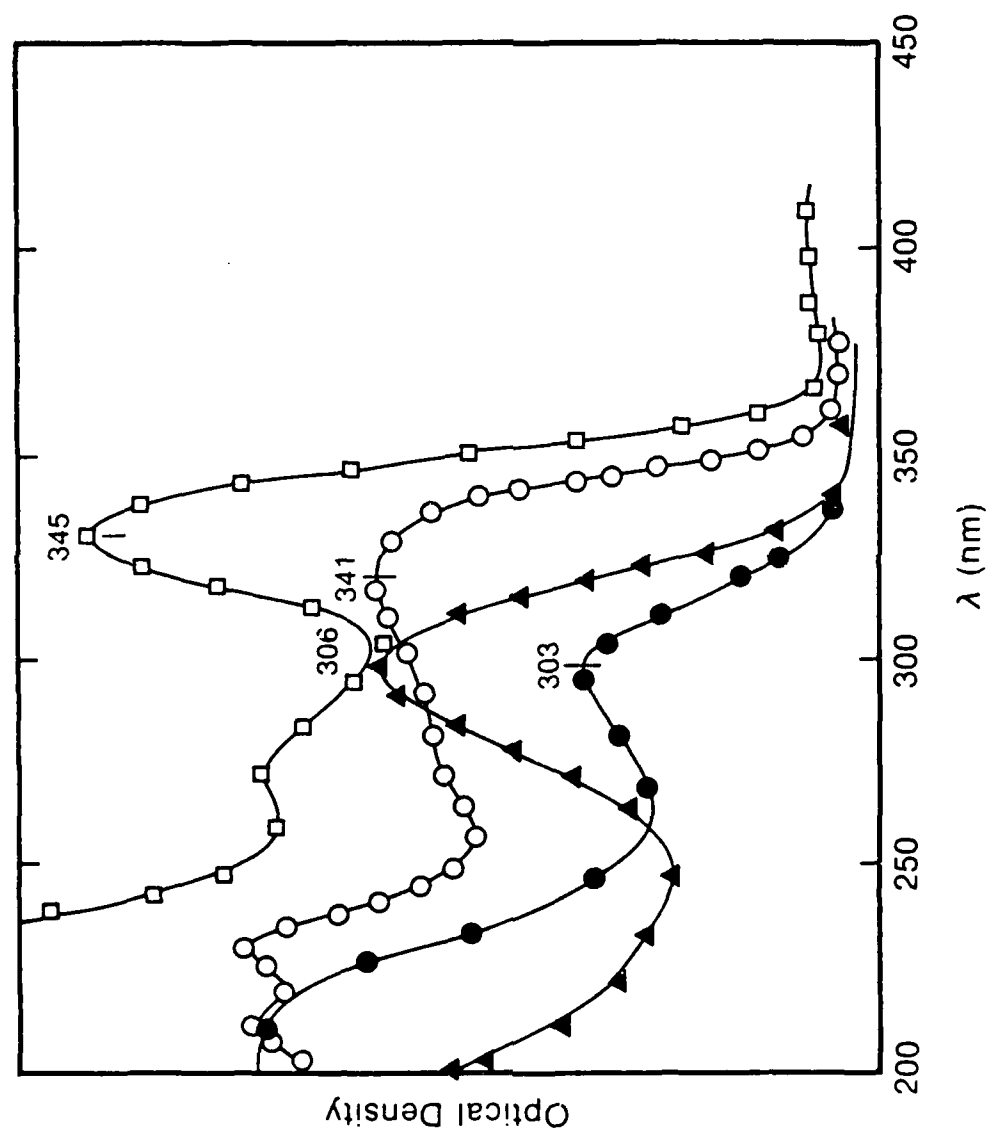


Figure 2. UV spectra of some typical polysilane films. (•-•-) poly(methyl phenethylsilane), (-Δ-Δ-) poly(methyl hexylsilane), (-O-O-) poly(phenylmethyl-co-dimethylsilane), -□-□- poly(phenyl methyl silane).

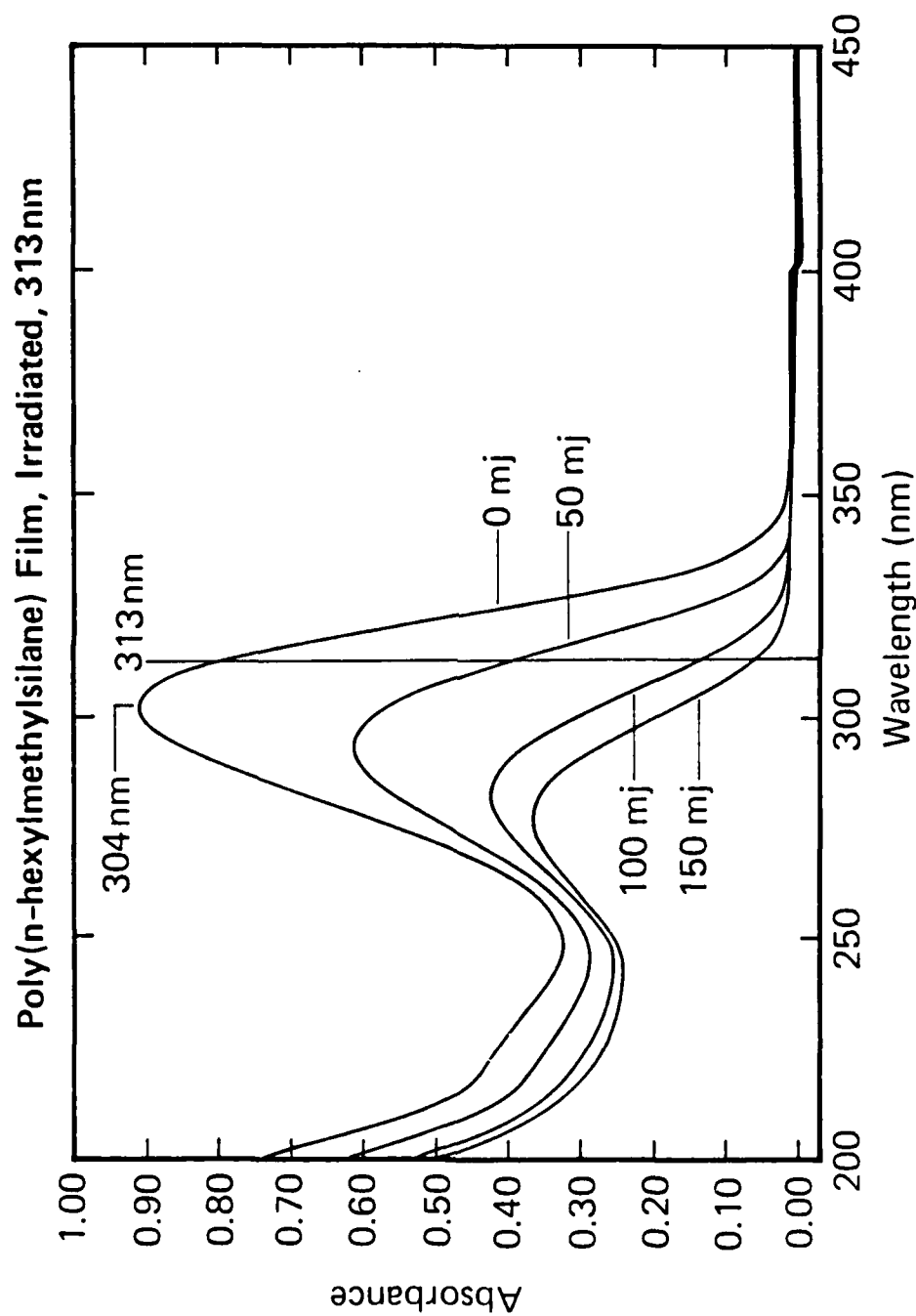


Figure 3. Photochemical bleaching of a film of poly(methyl hexylsilane) at 313 nm.



conventional

CEL

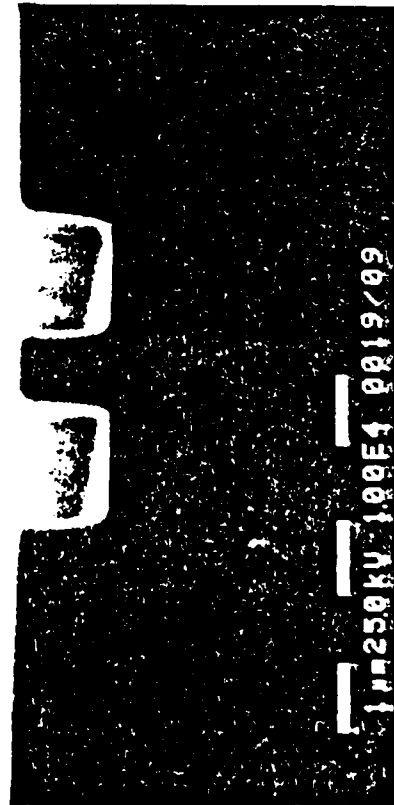
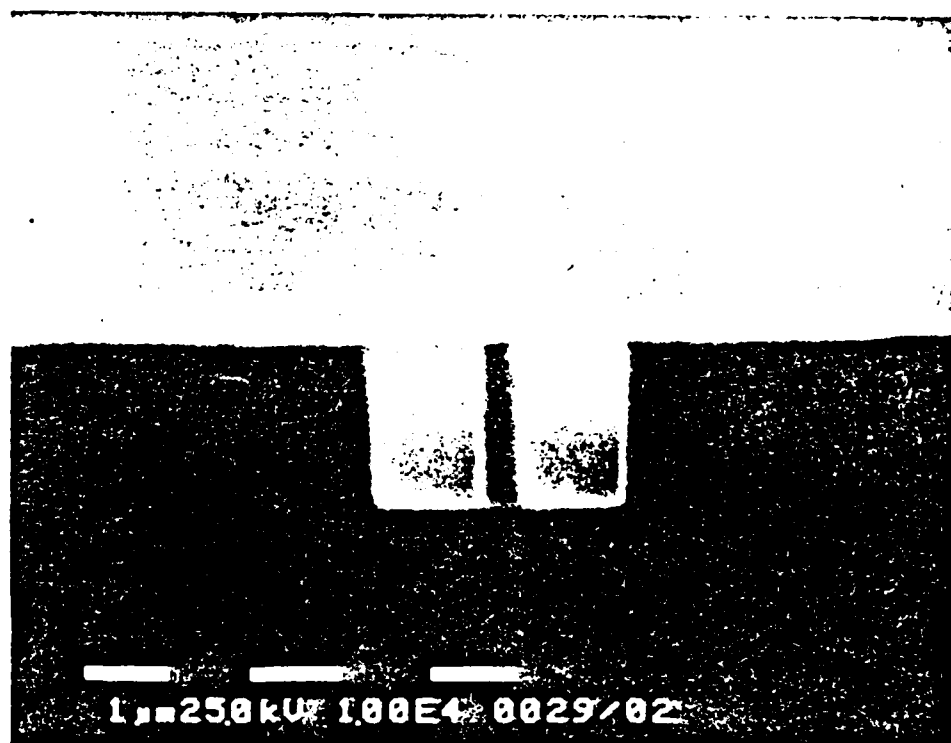


Figure 4. Contrast enhanced resist profiles from projection lithography at 313 nm. 0.2  $\mu\text{m}$  of poly(cyclohexylmethylsilane) over AZ-2400 photoresist, 110  $\text{mJ}/\text{cm}^2$  dose incident at photoresist surface.



**Figure 5.**  $0.75\ \mu\text{m}$  features generated in a bilayer of  $0.2\ \mu\text{m}$  of poly(cyclohexyl methylsilane) over  $2.0\ \mu\text{m}$  of a hardbaked Novolac-naphthoquinone-2-diazide photoresist;  $100\ \text{mJ}/\text{cm}^2$ ,  $\text{O}_2$ /RIE image transfer.

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